

Synthesis and Ring Structure of 7-Acetamido-7-deoxy-L-galacto-heptulose

Emma J. McDonald*

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7-Acetamido-7-deoxy-L-galacto-heptulose was prepared by oxidation of 1-acetamido-1-deoxy-D-glycero-D-galacto-heptitol with *Acetobacter suboxydans*. The new acetamido-deoxy-L-heptulose was shown to be a pyranose by comparison with β -D-fructopyranose. The following equations represent the optical rotation of 7-acetamido-7-deoxy- α -L-galacto-heptulopyranose in water at 20 °C and 3.5 °C, respectively:

$$[\alpha]^{20}_D = -15.5e^{-.0396t} - 97.1,$$

$$[\alpha]^{3.5}_D = -11.9e^{-.0101t} - 105.8,$$

where t is the time in minutes after dissolution of the sample.

1. Introduction

Several years ago, exploratory work in this laboratory, as well as work by others [1]¹, showed that *Acetobacter suboxydans* oxidizes certain acetamido-deoxy-D-alditols to the corresponding acetamidodeoxyketoses. According to the Bertrand-Hudson rule [2], one would expect *A. suboxydans* to produce 7-acetamido-7-deoxyheptuloses from eight 1-acetamido-1-deoxyheptitols. This paper reports the preparation and properties of a new heptulose, 7-acetamido-7-deoxy-L-galacto-heptulose, obtained by oxidation of 1-acetamido-1-deoxy-D-glycero-D-galacto-heptitol.

2. Results and Discussion

The new ketose (I) is closely related to D-fructose (II) and perseulose (III). The optical rotations and the magnitude and direction of the mutarotations given in table 1 can be used for the assignment of structure. Isbell and Pigman [3] established that crystalline D-fructose is a β -D-pyranose and that its mutarotation arises from a pyranose-furanose interconversion. The molecular rotation of I (-28,300) does not differ greatly from the molecular rotations of II (-23,800) and III (-21,400), but differs widely from the molecular rotation (+3,060) of D-fructofuranose (Hudson's " α -fruc-

TABLE 1. Optical rotation of certain ketoses

Ketoses	Temp	Specific rotation		k^a	$[\alpha]_D = Ae^{-kt} + C$	Sol. vent	References
		Initial	Final				
7-Acetamido-7-deoxy- α -L-galacto-heptulopyranose (I)	°C			min^{-1}			
	20	-112.6	-97.1	0.0172	$[\alpha]^{20}_D = -15.5e^{-.0396t} - 97.1$	H ₂ O	^b
	3.5	-117.7	-105.8	.0044	$[\alpha]^{3.5}_D = -11.9e^{-.0101t} - 105.8$	H ₂ O	^b
β -D-Fructopyranose (II)	20	-132.2	-92.4	.055	$[\alpha]^{20}_D = -39.8e^{-.1296t} - 92.4$	^c	[3]
	0	-132.9	-103.4	.0090	$[\alpha]^{0}_D = -29.5e^{-.0207t} - 103.4$	^c	[3]
α -L-galacto-Heptulopyranose (III) (perseulose)	20	-102	-86	.059	H ₂ O	[13]

^a $k = 1/t \log (r_0 - r_\infty)/(r - r_\infty)$. Measurements conducted as described in reference [12].

^b New measurement.

^c 0.001N potassium acid phthalate.

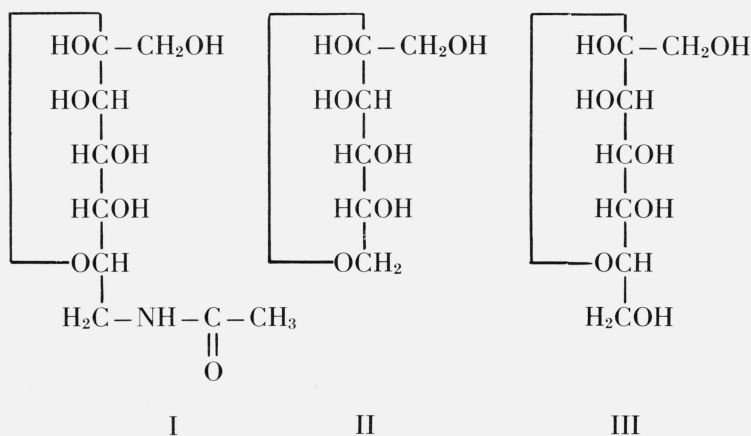
*Retired. Inquiries concerning this paper should be directed to the Division of Analytical Chemistry, National Bureau of Standards, Washington, D.C. 20234.

¹ Figures in brackets indicate the literature references at the end of this paper.

tose" [4]). One would expect small differences in molecular rotation because of differences in the substituents on C-6. The parallelism in the molecular rotations, however, is sufficient to indicate that the three compounds have similar structures. Compounds I, II, and III also show marked parallelism in the magnitude and direction of mutarotation. In each instance, the optical rotation decreases rapidly at a unimolecular rate. The rate for I (approximately one-third that for II and III) is not surprising because of the differences in the substituents on C-6. The effect of a change in temperature on the equilibrium rotation of I and II is much the same. In each instance, lowering the temperature shifts the equilibrium in the direction of the isomer known in the crystalline form. From these considerations (molecu-

lar rotation, mutarotation, and effect of temperature), it follows that I is a pyranose and that it has the configuration corresponding to that of β -D-fructopyranose. According to accepted nomenclature, anomers in the L-series having the same configuration for the anomeric carbon as a β -D-pyranose are designated as α -L-pyranoses, and I is named 7-acetamido-7-deoxy- α -L-galacto-heptulopyranose. Presumably, the mutarotation of I (like that of β -D-fructopyranose) arises from a pyranose-furanose interconversion.

The infrared absorption of I (fig. 1) shows bands at 6.02, 6.38, and 7.7 μ indicative of the free amido group. Hence, the nitrogen of the amido group is not part of a ring as it is in certain 5-acetamido-5-deoxypentoses [5 to 8].



- I. 7-Acetamido-7-deoxy- α -L-galacto-heptulopyranose.
 II. β -D-Fructopyranose.
 III. α -L-galacto-Heptulopyranose (perseulose).

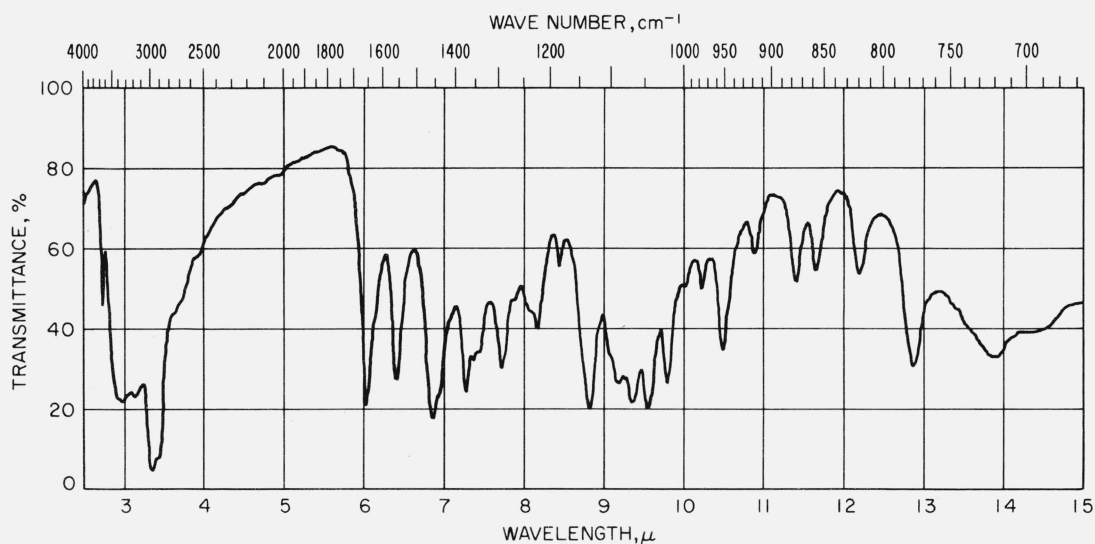


FIGURE 1. Spectrogram of 7-acetamido-7-deoxy- α -L-galacto-heptulopyranose in Nujol mull.

Several properties of the new 7-acetamido-7-deoxy-L-galacto-heptulose were determined for characterization. With 1-butanol:pyridine:water (3:2:1) as an ascending developing solvent, the mobility of the compound on Whatman No. 1 paper is 0.88 that of fructose. Color formation with staining reagents sensitive to ketones is as follows: phloroglucinol, violet; urea phosphate, yellow (bright yellow fluorescence); resorcinol, tan (violet fluorescence); orcinol, purple (red fluorescence). The compound reacts with Somogyi's copper-reducing reagent at approximately the same rate as fructose. It melts at 139 to 140 °C and yields a phenylosazone, mp 210 °C.

In conjunction with the synthesis of I, methods for the preparation of 1-amino-1-deoxyalditols were examined. Catalytic reduction of glycosylamines proved to be unsatisfactory because of the instability of the glycosylamines in neutral or slightly acid solution [9]. Reduction of sugar oximes [10] was satisfactory, and this method is recommended for small-scale preparations of 1-amino-1-deoxyalditols from readily available aldoses. Reduction of 1-nitro-1-deoxyalditols, prepared from the lower sugars by condensation with nitromethane [11], proved to be the most satisfactory method; reduction takes place readily and gives the amines in high yield.

3. Experimental Procedures

3.1. 1-Nitro-1-deoxy-D-glycero-D-galacto-heptitol

Nitromethane was condensed with α -D-mannose and the resulting 1-nitro-1-deoxy-D-glycero-D-galacto-heptitol and 1-nitro-1-deoxy-D-glycero-D-talo-heptitol were separated by the procedure of Sowden and Schaffer [11].

3.2. 1-Acetamido-1-deoxy-D-glycero-D-galacto-heptitol

A slurry consisting of 2 g of 1-nitro-1-deoxy-D-glycero-D-galacto-heptitol, 0.65 g of 10-percent palladium on carbon, and 50 ml of water was shaken for 1.5 hr, at room temperature, with hydrogen under a pressure of 30 psi. The resulting suspension was filtered, and the filtrate was evaporated to dryness under reduced pressure. A solution of the residue, crude 1-amino-1-deoxy-D-glycero-D-galacto-heptitol,² in 15 ml of warm water was cooled, treated with 2 ml of acetic anhydride, and filtered. Additional acetic anhydride (2 ml) was added to the filtrate, which was kept for 1.5 hr at room temperature and then treated with ethanol to the point of slight turbidity. After 20 hr, the resulting crystalline, 1-acetamido-1-deoxy-D-glycero-D-galacto-heptitol was separated and air-dried; yield, 1.65 g; mp, 200 °C (uncor); $[\alpha]^{20}_D = -15.5^\circ$ (c 2.1, water).

² In a separate experiment, the reduction product, on treatment with oxalic acid, gave the previously known [11] crystalline 1-amino-1-deoxy-D-glycero-D-galacto-heptitol oxalate, mp 193 to 195 °C with decomposition; $[\alpha]^{20}_D = -13.2^\circ$ (c 3.4, water). The direction of optical rotation was not given in the publication cited, but the compound is now shown to be levorotatory.

Anal. Calcd. for $C_9H_{19}NO_7$: C, 42.7; H, 7.6; N, 5.5. Found: C, 42.7; H, 7.4; N, 5.4.

3.3. 7-Acetamido-7-deoxy- α -L-galacto-heptulopyranose

1-Acetamido-1-deoxy-D-glycero-D-galacto-heptitol (5.1 g), D-mannitol (0.25 g), potassium dihydrogen phosphate (0.025 g), and yeast extract (0.25 g) were dissolved in 50 ml of water. Two 25-ml portions, in 125-ml flasks, were sterilized for 20 min in steam under a pressure of 20 psi, cooled, and inoculated with *A. suboxydans*. The reaction flasks were kept at 20 to 30 °C, and the reaction was followed by paper chromatography. After 10 days, the combined product was treated as follows: One ml of a 20-percent solution of zinc sulfate was added, and the mixture was neutralized to phenolphthalein with a saturated solution of barium hydroxide. The suspension was filtered, and the filtrate was deionized with a mixture of cation- and anion-exchange resins, and evaporated to dryness. The residue was extracted with 80-percent aqueous methanol; the solid material (unoxidized 1-acetamido-1-deoxy-D-glycero-D-galacto-heptitol) was removed by filtration, and the filtered solution was evaporated under reduced pressure. The residue was dissolved in water and lyophilized to remove all solvent. The solid material was dissolved in a minimal amount of methanol, and ethyl ether added to the point of incipient turbidity. After several weeks, crystalline I separated. The compound was recrystallized from methanol; yield, 3.18 g; mp, 139 to 140 °C. The substance exhibits the mutarotation represented in table 1. $[\alpha]^{20}_D = -112.6^\circ$ initially, and -97.1° at equilibrium; $[\alpha]^{3.5}_D = -117.7^\circ$ initially and -105.8° at equilibrium (c 3.3, water).

Anal. Calcd. for $C_9H_{17}NO_7$: C, 43.02; H, 6.82; N, 5.58. Found: C, 43.15; H, 6.85; N, 5.6.

3.4. 7-Acetamido-7-deoxy-L-galacto-heptulose Phenylosazone

7-Acetamido-7-deoxy-L-galacto-heptulose (200 mg), phenylhydrazine (35 mg), acetic acid (200 mg), and water (5 ml) were heated in a boiling-water bath for 2 hr. The resulting phenylosazone was separated by filtration and washed successively with dilute acetic acid, 95-percent ethanol, and ether; yield, 243 mg. After recrystallization from ethanol, the phenylosazone melted with decomposition at 209 °C.

Anal. Calcd. for $C_{21}H_{27}N_5O_5$: C, 58.7; H, 6.3; N, 16.3. Found: C, 58.1; H, 6.3; N, 16.1.

3.5. 7-Acetamido-7-deoxy-L-galacto-heptulose Phenylosotriazole

The phenylosazone of I (191 mg) was refluxed for 2 hr with a solution prepared from 121 mg of copper sulfate pentahydrate and 15 ml of water. The hot suspension was filtered to remove cuprous oxide and unreacted phenylosazone, and the filtrate was passed

through a column of mixed cation- and anion-exchange resins. After the eluate had been evaporated under reduced pressure, the phenylosotriazole of I crystallized; the compound was recrystallized three times from hot water; mp, 210 °C.

Anal. Calcd. for $C_{15}H_{20}N_4O_5$: C, 53.6, H, 5.99. Found: C, 53.6; H, 5.5.

The author expresses her appreciation to H. S. Isbell for suggesting the research problem and for highly valued counsel, and to R. J. Hall and J. K. Taylor for microanalyses.

(Paper 69A3-349)

4. References

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Publications of the National Bureau of Standards*

Selected Abstracts

Excitation of acoustic waves in plasmas, W. A. Saxton, *Radio Sci. J. Res. NBS/USNC-URSI*, **69D**, No. 4 (Apr. 1965).

This paper reports early results in an experimental study to determine the effects of perturbing weakly ionized gaseous plasmas with acoustic waves emanating from transducers that operate in the audio and ultrasonic frequency ranges. Compact loudspeakers incorporated into cylindrical plasma discharge tubes provide the source of acoustic signals. Modulation of electromagnetic waves by the acoustically-disturbed plasma is measured in a unique rectangular cavity whose output is detected and fed to a wave analyzer. Resultant wave-analyzer responses indicate that the collision frequency is modulated in addition to the plasma frequency, and suggest that the variations in both are proportional to the magnitude of loudspeaker diaphragm deflection, as predicted by simple acoustic theory. Knowing that two forms of modulation occur simultaneously, a calibration scheme was developed to separate the variation Δf_p in the plasma frequency from the total response. Measurements to date indicate that $\Delta N_e/N_e = \Delta N/N$ (where N_e and N are electron and neutral-molecule densities, respectively) for slightly-ionized gases which are subjected to low-frequency pressure variations in the order of 10^{-5} mm Hg, and that such variations produce plasma-frequency perturbations of 0–140 kc/s at plasma frequencies up to 800 Mc/s.

Wave interaction in oxygen magnetoplasmas, K. V. Narasinga Rao, *Radio Sci. J. Res. NBS/USNC-URSI*, **69D**, No. 4 (Apr. 1965). Electron cyclotron resonance absorption of microwaves in decaying oxygen magnetoplasmas is utilized to alter the plasma parameters such as the "temperature" and number density of the electrons. The technique of cross modulation of microwaves in partially filled plasma waveguides is used in this investigation. It is shown that for small amplitudes (~ 120 mW at 5.3 Gc) of the resonant heating signal the inelastic collision of low energy electrons introduce a barrier for rapid heating the electron gas. For higher incident amplitudes (~ 500 mW at 5.3 Gc), not only does rapid heating of the electron gas occur, but also additional electron production and loss mechanisms are observed. The implications of these results on (a) apparent discrepancies in measurements of attachment coefficient by microwave methods, and (b) control of ionospheric plasma parameters by radio wave absorption are discussed.

Test of the constancy of the velocity of electromagnetic radiation in high vacuum, P. Beckmann and P. Mandics, *Radio Sci. J. Res. NBS/USNC-URSI*, **69D**, No. 4 (Apr. 1965).

It is pointed out that Einstein's postulate of the constant velocity of light is verified only indirectly by elementary-particle experiments leaning more or less heavily on present electromagnetic theory, the latter being verified only for low velocities. Direct experiments can be explained by the ballistic theory of light if transparent media, such as gases, reradiate as a secondary source. A direct experiment with coherent light reflected from a moving mirror was performed in vacuum better than 10^{-6} torr. Its result is consistent with the constant velocity of light.

Transmission and reflection of electromagnetic waves by a hot plasma, E. C. Taylor, *Radio Sci. J. Res. NBS/USNC-URSI*, **69D**, No. 5, (May 1965).

The relativistic form of the Vlasov equation is used to solve the problem of transmission and reflection of normally incident electromagnetic waves. Transmission and reflection coefficients are derived for a plasma half-space and for a plasma slab, using the assumption that electrons are specularly reflected at the boundaries. These coefficients are functions of the ratio of the electron thermal speed to the vacuum speed of light, indicating that temperature

dependence in these cases is a relativistic effect. Nevertheless, it is seen that the nonrelativistic limits of these coefficients differ from those obtained by using the cold-plasma equations since the transition to the zero-temperature limit has a nonuniform character.

Microwave spectral tables. Diatomic molecules, P. F. Wacker, M. Mizushima, J. D. Petersen, and J. R. Ballard, *NBS Mono.* 70, (Dec. 1, 1964) \$2.00.

For about 1500 spectral lines of diatomic molecules observed by coherent radiation techniques, measured frequencies, assigned molecular species, assigned quantum numbers, and newly computed intensities are given. Molecular data, such as rotational constants, dipole moments, and various coupling constants, determined by such techniques, are also tabulated, as are other molecular constants used in the intensity computations. References are given for all included data. For determination of hyperfine spectra, both Casimir's function and the intensity splitting factor are given for both integral and half-integral quantum numbers J and I , permitting application to additional molecules with unclosed electronic shells and with hyperfine splitting produced by more than one nucleus.

Microwave spectral tables. Line strengths of asymmetric rotors, P. F. Wacker and M. R. Pratto, *NBS Mono.* 70, Vol. II (Dec. 15, 1965) \$3.00.

Line strengths of asymmetric rotors are tabulated as a function of Ray's asymmetry parameter κ for rotational quantum numbers J from 0 to 35. Procedures for interpolation as a function of κ and extrapolation to larger J values are discussed.

On the statistical theory of electromagnetic waves in a fluctuating medium (II) Mathematical basis of the analogies to quantum field theory, K. Furutsu, *NBS Mono.* 79 (Dec. 7, 1964) 35 cents.

Many analogies to quantum field theory are inherent in the statistical theory of waves. This is due to the fact that basic equations exist in the latter theory which correspond closely to the fundamental equations of the former theory; i.e., to the commutation relations and the Heisenberg equation of motion. A probability density function of waves is introduced here which corresponds to the probability amplitude function in quantum mechanics. The boundary conditions at infinity for this probability density function are then found to be expressed in the same form as the vacuum boundary conditions in field theory. The theory of the statistical Green's functions and their relationships to the expectation values of the physical variables is also extensively developed, using auxiliary external sources of the wave and of the fluctuating medium. It is found that there exists a one-to-one correspondence between the formalism of Green's functions presented here and that used in field theory. The above correspondence may be important for a further development of the statistical theory of waves, just as the advanced techniques of field theory have greatly influenced the development of thermodynamics (or statistical physics).

On the formulation and numerical evaluation of a set of two-phase flow equation modelling the cooldown process, S. Jarvis, Jr., *NBS Tech. Note* 301 (Jan. 4, 1965) 55 cents.

A model of transient two-phase flow in a pipe is constructed in Eulerian coordinates assuming a single velocity but independent temperatures in the two phases. Experiments on the numerical integration of the system for cooldown problem by both Lax and Courant-Isaacson-Rees methods indicate that a very fine spatial difference net must be used to compensate for the numerical diffusion essential to computational stability if a second surge is to be realized.

Angular momentum distribution and emission spectrum of OH ($^2\Sigma^+$) in the photodissociation of H_2O , T. Carrington, *J. Chem. Phys.* **41**, No. 7, 2012–2018 (Oct. 1, 1964).

When water vapor absorbs light of wavelength less than 1350 Å, an electronically excited OH fragment may be produced. This process has been observed, using wavelengths 1216 Å, 1236 Å, and 1302 Å, and the rotational and vibrational excitation of the product $\text{OH}^2\Sigma^+$ has been determined from its emission spectrum. Most of the energy beyond that necessary to produce electronically excited OH goes into rotation of that molecule. Roughly one-third of the OH molecules have one quantum of vibrational energy, and in these molecules too, the highest energetically allowed rotational levels are strongly populated. Knowledge of the energy and rotational angular momentum of the OH allows estimation of the kinetic energy and orbital angular momentum of the H as it flies away from the center of mass. This is interpreted in terms of a two body interaction at large distances.

Morphology of thermally evaporated zinc cleavage surfaces,

A. W. Ruff, Jr., *J. Chem. Phys.* **41**, No. 5, 1204–1213 (Sept. 1, 1964).

The process of thermal evaporation has been studied on (0001) cleaved zinc surfaces. The effects on the evaporated surface structures due to zinc vapor undersaturation, impurities, and crystal dislocations were investigated. For undersaturation ratios between 0.29 and 0.006, evaporation proceeded primarily from localized surface regions resulting in shallow conical evaporation pits. The number density of these evaporation pits was in good agreement with the dislocation density determined by chemical etching. It was concluded that the step sources responsible for the evaporation pits were dislocations terminating at the surfaces. The theory of evaporation from dislocation sites predicts a critical undersaturation similar to that observed experimentally. The interferometrically measured evaporation pit slopes increased with vapor undersaturation in agreement with the theory of Cabrera and Levine near the critical undersaturation. The data extended further into the region of higher undersaturations. The effects of surface impurities were studied by admitting oxygen into the evaporation cell. For a constant vapor undersaturation, the evaporation pit slopes increased at the higher oxygen pressures. This increase could be explained qualitatively in terms of a reduction in step velocity.

Statistical surface thermodynamics of simple liquid mixtures, C. A. Eckert and J. M. Prausnitz, *A. I. C. H. E. J.* **10**, No. 5, 677–683 (Sept. 1964).

The surface properties of nonpolar liquid mixtures are derived from the application of the grand partition function to a cell model of the vapor-liquid interface. The surface tension and the surface composition are expressed in terms of the activity coefficients in the bulk liquid and pure-component properties. The results are in excellent agreement with existing data for the surface tension of mixtures. This treatment provides a sound theoretical basis for the prediction of surface properties of other liquid systems, and is especially applicable to cryogenic mixtures.

The accurate measurement of voltage ratios of inductive voltage dividers, T. L. Zapf, *Acta IMEKO*, pp. 317–331 (1964).

Several methods have been developed at the National Bureau of Standards for the very accurate measurement of audio frequency voltage ratios associated with inductive voltage dividers. Uncertainties in voltage ratio of less than 2×10^{-7} have been obtained in measurements with transformer-type capacitance bridges. The attainment of such accuracy has provided a firm base for further investigations on inductive voltage dividers. An inherent major error arises from the interaction between distributed shunt impedances and leakage impedances in the windings. In specific designs of inductive voltage dividers the relative magnitudes of such errors are calculable and are characteristic of the design. A divider may be completely characterized by the designation of the characteristic relative errors combined with an absolute measurement. A method involving complementary measurements has been developed to yield an absolute measurement of the inphase and quadrature components of the voltage ratio characteristic. Single-decade inductive voltage dividers have been constructed with ratio magnitude characteristics and residual errors less than 5×10^{-8} . This recent work has verified the accuracy of measurements made by other methods.

Correlation factors for impurity diffusion—Bcc, diamond, and Fcc structures, J. R. Manning, *Phys. Rev.* **136**, No. 6A, A1758–A1766 (Dec. 14, 1964).

A general equation for the impurity correlation factor is derived in terms of effective escape frequencies. This equation applies even when the vacancy jump frequency for association of a vacancy-impurity complex differs from the frequency far from an impurity. Parameters in this equation are calculated for body-centered cubic, diamond, and face-centered cubic structures. In these calculations, it is assumed that vacancy jumps which do not involve a nearest neighbor of the impurity are unaffected by the impurity but that association and dissociation jumps, which do involve nearest neighbors of the impurity, are affected. Analytical expressions for the correlation factor in terms of vacancy jump frequency ratios are obtained. In the bcc and fcc structures, results are given for two cases: (A) where all dissociative jumps are equally likely, and (B) where a vacancy which makes a dissociative jump to a second nearest neighbor site is still partially bound to the impurity but vacancies which make dissociative jumps to other sites are not. In the diamond structure, case A cannot be distinguished from case B. Results for the diamond structure and for case A in the fcc structure differ only slightly from previous more approximate results. A comparison is made between the present random walk method of calculating correlation factors and the pair association method.

Thermal decomposition of some alkyl halides by a shock-tube method, W. Tsang, *J. Chem. Phys.* **41**, No. 8, 2487–2494 (Oct. 15, 1964).

The decomposition of several alkyl halides have been studied by a comparative rate method using a single pulse shock tube. Rate constants for the elimination of hydrogen halide from the parent molecule are compared with the rate of elimination of hydrogen bromide from isopropyl bromide. The Arrhenius expression for the latter reaction has previously been found to be $k(i\text{-C}_3\text{H}_7\text{Br}) = 10^{13.62}e^{-47,800/RT}$ (sec^{-1}). On this basis, the following rate expressions have been obtained:

$k(\text{C}_2\text{H}_5\text{Br}) = 10^{13.19}e^{-53,700/RT}$ (sec^{-1})	740–940 °K
$k(\text{C}_2\text{H}_5\text{Cl}) = 10^{13.16}e^{-56,460/RT}$ (sec^{-1})	820–1000 °K
$k(i\text{-C}_3\text{H}_7\text{Cl}) = 10^{13.64}e^{-51,100/RT}$ (sec^{-1})	750–950 °K
$k(i\text{-C}_3\text{H}_7\text{I}) = 10^{13.67}e^{-45,065/RT}$ (sec^{-1})	680–850 °K
$k(t\text{-C}_4\text{H}_9\text{I}) = 10^{13.73}e^{-38,080/RT}$ (sec^{-1})	650–760 °K

These results are compared with the results of earlier low temperature studies. The advantages and reliability of this type of kinetic study are discussed.

Relaxation of a Lorentz gas with repulsive r^{-s} force law, H. Oser, K. E. Shuler, and G. H. Weiss, *J. Chem. Phys.* **41**, No. 9, 2661–2666 (Nov. 1, 1964).

The relaxation of a Lorentz gas (dilute light particle subsystem in a heavy particle heat bath) has been studied for a repulsive r^{-s} central force law interaction between the light and heavy particles. The Fokker-Planck equation for the velocity distribution functions of the light particle subsystem has been solved numerically for $s = 5, 9, 13, 21$ and ∞ for various initial conditions. The dependence of the rate of relaxation and of the form of the time dependent velocity distribution function on the force law parameter s is discussed in light of the above results.

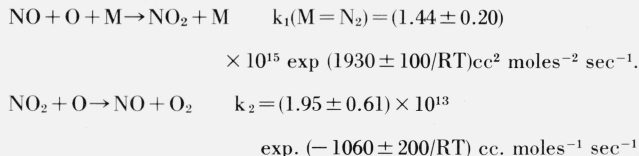
Modulus of rupture of glass in relation to fracture pattern, M. J. Kerper and T. G. Scuderi, *Am. Ceramic Soc. Bull.* **43**, No. 9, 622–625 (Sept. 7, 1964).

Glass broken in flexure shows a fracture face which normally consists in part of a smooth area that includes the fracture origin. The area of this smooth portion of "mirror" has been found to bear a relationship to the magnitude of the stress causing rupture. This relationship has been studied for eight glasses tested under a variety of conditions. It was observed that the conditions of the glass surface, the test temperature, difference in exposure time to test temperature, and rate of loading, all had an effect on the strength of glass but did not affect the relationship between modulus of rup-

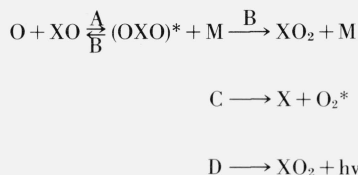
ture and the mirror size. The composition did, however, affect this relationship. This relationship is generally expressed as a power function where the modulus of rupture times the radius of the mirror to the one half power is equal to a constant. This expression is not, however, valid for the full range of the data.

Mass-spectrometric study of the reactions of O atoms with NO and NO₂, F. S. Klein and J. T. Herron, *J. Chem. Phys.* **41**, No. 5, 1285-1290 (Sept. 1, 1964).

The reaction of O atoms with NO and NO₂ have been studied using a mass spectrometer to directly measure the O atom partial pressure. The results obtained are as follows:



These reactions are discussed in terms of the general mechanism



From the overall rate constants and previous results on the isotopic exchange rates of O¹⁸ with O₂, NO, and NO₂ (J. T. Herron and F. S. Klein, *J. Chem. Phys.* (1964)) the rates of the elementary reaction steps have been calculated.

Infrared studies of the photolysis of HN₃ in inert and reactive matrices. The infrared spectrum of NH, D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **49**, No. 9, 2838-2841 (Nov. 1, 1964). Infrared and ultraviolet observations have been made on the products of the photolysis of HN₃ and DN₃ suspended in Ar, N₂, and CO₂ matrices at 4, 14, and 20 °K. Appreciable concentrations of NH (ND) in the ground (—) state are produced. The vibrational fundamental of NH has been observed directly at 3133 ± 2 cm⁻¹ in Ar and N₂ matrices. The identification of H atoms in the photolysis of HN₃ requires that some of the HN₃ molecules undergo photolytic rupture at the H—N bond. Consideration is given to the secondary reactions which occur between NH and itself or HN₃. It appears likely that HN=NH and/or HN=N—N=NH may contribute to the observed products of these secondary reactions.

Contributions to the theory of shell corrections, U. Fano and J. E. Turner, *ch. 4, 49-67, Nuclear Sci. Series Report No. 39, Natl. Acad. Sci.-Natl. Res. Council Publ.* 1133 (1964).

Sum rules pertaining to the inelastic form factor $F_n(\mathbf{q})$ are calculated and applied to the evaluation of shell corrections to the stopping power formula, to order $1/v^4$ in the velocity of the incident particle. Details are given pertaining to the evaluation of the shell corrections in the paper reproduced in Appendix A. Comments are presented regarding the possible generality of a Lindhard-Winther equipartition rule.

Electrode potentials in fused system. VIII. Oxidation kinetics of silver in sodium chloride, K. H. Stern and W. E. Reid, Jr., *J. Phys. Chem.* **68**, No. 12, 3757-3764 (Dec. 1964).

The oxidation rate of metallic silver in molten sodium chloride has been studied by a galvanic cell technique as a function of oxygen partial pressure, 0-1st and temperature (800-900 °K). The results are accounted for by two forward reactions: (A) $2\text{Ag} + \frac{1}{2} \text{O}_2 \rightleftharpoons 2\text{Ag}^+ + \text{O}^{2-}$, (B) $\text{Ag}^0 + \text{Na}^{+k_2} \rightleftharpoons \text{Ag}^+ + \text{Na}^0$. k_1 is a linear function of p_0 in the range $0 < p \leq 1$ atm. For $p_0 = 1$ at 870° $k_1 = 11.9 \times 10^{15}$, $k_2 = 0.35 \times 10^{152}$ atoms cm⁻² sec⁻¹. With increasing time $d[\text{Ag}^+]/dt$ decreases because of the reverse of reaction (A), for which

$k_3 = \frac{k_1 + k_2}{K_{\text{A}} p_0^{1/2}}$, where K_{A} , the equilibrium constant for (A), is 8.3×10^{-7} on the mole fraction scale. The general differential equation for

this system is derived and numerically integrated. The mechanism of the reaction is discussed in terms of absolute reaction rate theory. It is concluded that the rate determining step for (A) is the chemisorption of O₂, which is hindered by an adsorbed layer of chloride ions, and that for (B) the formation of Ag⁺ is rate-determining.

Election scattering without atomic or nuclear excitation, J. W. Motz, H. Olsen, and H. W. Koch, *Rev. Mod. Phys.* **36**, No. 4, 881-928 (Oct. 1964).

This survey is concerned with the process of single electron scattering by an atom without excitation of the atom or the nucleus. Results are given which pertain to the kinematics, the radiative effects, the polarization behavior, and the cross sections for this process over a wide range of electron energies extending from the nonrelativistic (> 10 kev) to the extreme relativistic regions.

K-ionization cross sections for relativistic electrons, J. W. Motz and R. C. Placious, *Phys. Rev.* **136**, No. 3A, A662-A665 (Nov. 2, 1964).

Experimental values of the K-shell ionization cross section are determined from scintillation spectrometer measurements of the K x rays emitted when thin targets of tin and gold are bombarded by 50, 100, 200, and 500 keV electrons. For these energies and atomic numbers, the experimental results show differences with the cross sections given by Burhop's nonrelativistic calculations and by Perlman's relativistic calculations, but show good agreement with the predictions of Arthurs and Moiseiwitsch who employed relativistic free particle wave functions for the projectile electron and nonrelativistic wave functions for the atomic electron.

Tables of energy losses and ranges of electrons and positrons, M. J. Berger and S. M. Seltzer, *Natl. Aeronaut. Space Admin. NASA SP-3012, I-127* (1964).

Tables are presented for approximately forty materials, and energies between 10 kev and 1000 Mev, which contain the following information: mean energy loss of electrons by collisions with atomic electrons and by bremsstrahlung, the mean range, and the radiation yield (conversion of electron kinetic energy into bremsstrahlung energy). Auxiliary tables contain information about restricted collision losses in water, critical energies (at which the collision and bremsstrahlung losses are equal), and electron-positron differences in regard to energy loss and range. Some comparisons are made between calculated and experimental values of the mean energy loss.

Tables of energy losses and ranges of heavy charges particles, W. H. Barkas and M. J. Berger, *Natl. Aeronaut. Space Admin. NASA SP-3013, I-131* (1964).

Two-variable proton stopping power and range tables are given as functions of the particle energy τ and of the mean excitation energy I_{adj} of the medium, for 160 values of τ between 1 and 5000 Mev, and for 36 values of I_{adj} . These tables can be applied to any medium with specified mean excitation energy. By simple scaling, they can also be applied to other heavy particles with mass and charge different from that of the proton. The tabulated values below 8 Mev are based on experimental stopping-power and range data as summarized by a 9-parameter least-squares range formula. Above 8 Mev they are based on the Bethe stopping power theory, except for the shell corrections which are calculated by an empirical formula in the variables τ and I_{adj} derived from the analysis of experimental data.

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